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(54) IMPROVEMENTS IN THE PROCESING OF THERMOPLASTIC MATERIAL

(71) We, NEYNABER CHEMIE GMBH, a German Company, of 2854, Loxstedt, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to improvements in the processing and especially the shaping of thermoplastic material.

Shaping of thermoplastic synthetic materials is carried out according to known processes such as calendering, moulding, injection moulding and extruding at an elevated temperature. One of the difficulties which occurs during this shaping process is the sticking of the plastic masses to parts of the machine being used. Attempts have been made to overcome this difficulty by the addition of release agents to the thermoplastic materials. A large number of release agents has already been proposed which are intended to prevent the thermoplastic masses from sticking during the shaping process. These products include paraffins of various molecular weight and degree of branching of the chains, higher molecular weight aliphatic monocarboxylic acids of natural and synthetic origin, and amides derived therefrom, metal soaps and simple esters. Carnauba wax and beeswax may be mentioned as esters of natural origin. The synthetic esters proposed as release agents are obtained by esterification of aliphatic monocarboxylic acids having a chain length of at least 12 carbon atoms with mono- or poly-hydric alcohols. These products include, for example, ethyl palmitate, butyl stearate, octyl stearate, ethylene glycol monostearate, ethylene glycol distearate, butylene glycol dimontanate, and glycerine monooleate. Esters of polycarboxylic acids with long-chain aliphatic monohydric alcohols have also already been proposed as release agents for example dioctyl sebacate, for the shaping of thermoplastic masses based on polyamides.

These previously suggested release agents, and especially the products derived from long-chain aliphatic carboxylic acids, still leave much to be desired in respect to technical processing. They do bring about an improved flowability of the plastic masses to be processed, but they do not prevent sufficiently their sticking to the hot metal parts of the processing machines.

Attempts have been made to eliminate this drawback by the use of new release agents or release agent compositions so as to obtain a satisfactory freedom from sticking during the shaping, especially during the processing of chlorine-containing polymerisates, as for example, polyvinyl chloride, which are particularly susceptible. Thus, combinations of paraffins with silicones were suggested as release agents. These indeed led to an adequate freedom from sticking during the shaping, but they form a continuous film on the surface of the shaped semi-finished or finished products, which makes a subsequent processing or treatment, for example welding, glueing, printing, lacquering etc. very difficult or quite impossible. This exudation effect occurs even with addition of very small amounts of release agent, for example 0.1%.

The present invention therefore provides a method of preventing sticking of thermoplastic synthetic material to parts of apparatus during processing of said thermoplastic material comprising adding to a mass of said thermoplastic material prior to processing 0.01 to 5% by weight based on the thermoplastic material of a release agent mixed ester having a hydroxyl and an acid number of from 0 to 6 and which is obtained from (a) an aliphatic, cycloaliphatic and/or aromatic dicarboxylic acid, (b) an aliphatic polyol and (c) an aliphatic monocarboxylic acid having from 12 to 30 carbon atoms in the molecule.

With the method according to the invention it is possible to impart to most thermoplastic materials a sufficient freedom from sticking, even for the relatively long lasting

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case of a shaping operations, without the formation of a troublesome exuded film taking place.

Release agents comprising mixed esters with hydroxyl and acid values of 0 to 6 from (a) aliphatic, cycloaliphatic and/or aromatic dicarboxylic acids with 2 to 22 carbon atoms in the molecule, (b) aliphatic polyols with 2 to 6 hydroxyl groups in the molecule and (c) aliphatic monocarboxylic acids with 12 to 30 carbon atoms in the molecule are particularly suitable.

These mixed esters constructed according to the invention provide a very good freedom from sticking, even in very small amounts, for example 0.1%. Their effectiveness as release agents increases as the amount added is increased, without giving rise to the exudation phenomena even when relatively high amounts are added, and therefore to an impairment of the later further processing of the shaped semi-finished or finished parts.

The molar ratio of dicarboxylic acid to polyol to monocarboxylic acid in the mixed esters according to the invention can vary, while it has proved advantageous for the production of products with the desired properties to keep to a ratio of dicarboxylic acid: polyol: monocarboxylic acid of (n-1): n: nm-2(n-1). In this formula, n represents a whole number from 2 to 11 and m represents the functionality of the polyol used, and thus may assume values from 2 to 6. A small deviation from these proportions is possible as long as mixed esters are still obtained whose hydroxyl and acid values do not exceed the value 6. The character of the mixed esters, whether of low or high molecular weight, is largely determined by the value of n, higher molecular weight products being obtained with higher values of n.

Mixed esters based on adipic acid, pentaerythritol and stearic or oleic acid, in which the proportion of adipic acid: pentaerythritol: stearic/oleic acid amounts to (n-1): n: 4n—2(n-1), n representing values of from 2 to 8 in the case of stearic acid and 2 to 7 in the case of oleic acid, have proved specially suitable. Such preferred products have, for example, in the case of stearic acid, a proportion of the mixed ester components adipic acid: pentaerythritol: stearic acid of 1 : 2 : 6 or 2 : 3 : 8 or 4 : 5 : 12 or 6 : 7 : 16 or 7 : 8 : 18, and in the case of oleic acid a proportion of adipic acid: pentaerythritol: oleic acid of 1 : 2 : 6 or 3 : 4 : 10 or 5 : 6 : 14. A further preferred form of this latter product has an adipic acid: pentaerythritol: oleic acid ratio of 4 : 5 : 12.

The preparation of the release agents to be used according to the invention is effected by known esterification processes by, for example, esterifying long-chain aliphatic monocarboxylic acids with di- or poly-hydric polyols so that the part ester obtained still contains one or more free hydroxyl groups and these hydroxyl groups are then reacted with the corresponding dicarboxylic acids. However, a part of the hydroxyl groups of a polyol can first be esterified with a dicarboxylic acid and then the remaining free hydroxyl groups of the part ester obtained can be reacted with relatively long-chain aliphatic monocarboxylic acids. In such case the starting substances may be used in various mutual proportions for the preparation of the mixed esters, but under the conditions that the total numbers of the carboxyl functions and the hydroxyl functions in the starting substances are equal. The mixed esters obtained according to the invention then contain practically no free carboxyl or hydroxyl groups and possess hydroxyl and acid numbers from 0 to 6.

In the simplest case, for example, 1 mol of a dicarboxylic acid, 2 mol of an n-functional polyol and 2n-2 mol of a monocarboxylic acid are esterified according to known processes, preferably in two stages. Two variants are thereby possible. In the first variant, 1 mol of a dicarboxylic acid is esterified with 2 mol of the polyol in the first stage until the acid number is practically nil. Then in the second stage the product is esterified with the stoichiometric amount of monocarboxylic acid required until practically no free hydroxyl and carboxyl groups are present, that is, the OH number and acid number assume values between 0 and 6.

In the second variant, in the first stage two mols of an n-functional polyol is esterified with 2n-2 mol of a long-chain monocarboxylic acid until the acid number is practically nil. Then in the second stage the product is exhaustively esterified with 1 mol of a dicarboxylic acid, so that the mixed ester obtained has practically no free hydroxyl or carboxyl groups, that is, its OH number and acid number assume values from 0 to 6. Apart from this, it is also possible to carry out the formation of the mixed ester from the starting components in a one-stage process.

Besides the low molecular weight products the preparation of which is previously described, the mixed esters utilisable as release agents according to the invention also include high molecular weight compounds. These can be prepared by selecting as the molar proportion of the polyol to the dicarboxylic acid one less than 2 : 1, but not less than 1 : 1, for example 5 : 4 or 7 : 6. The excess of hydroxyl functions remaining to these components in the polyester formation is esterified by an equivalent amount of saturated or unsaturated long-chain aliphatic monocarboxylic acid or a mixture of long-chain monocarboxylic acids, so that again mixed esters are formed which contain practically no free hydroxyl or carboxyl groups. The formation of ester from the starting substances may also in this case be carried out either in a two-

stage process or in one stage. These high molecular weight poly-mixed esters possess an extra-ordinarily low vapour pressure at the processing temperatures usual for the shaping of thermoplastic synthetic materials. For this reason the release agents to be used according to the invention based on high molecular weight mixed esters are particularly valuable for use in the shaping of thermoplastic synthetic materials.

The following compounds are suitable as starting substances for the preparation of the mixed este s of both low- and high-molecular weight compounds to be used as release agents according to the invention: for example, oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, nonanedicarboxylic, undecanedicarboxylic, eicosanedicarboxylic, maleic, fumaric, citraconic, mesaconic, itaconic, cyclopropane1,2-dicarboxylic, cyclobutane-1,2- and -1,3-dicarboxylic, cyclopentane-1,2-dicarboxylic, camphoric, hexahydrophthalic, phthalic, terephthalic, isophthalic, naphthalic, or diphenyl-o,o'-dicarboxylic acids.

Polycomponents for the preparation of the mixed esters may include, for example, the following compounds: ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol, 2,3-butanediol, 1,5-butanediol, 1,6-hexanediol, glycerine, trimethylolpropane, erythritol, pentaerythritol, dipentaerythritol, xylitol, mannitol or sorbitol.

Examples of long-chain aliphatic monocarboxylic acids which are suitable for the preparation of the mixed esters used according to the invention include: lauric, tridecylic, myristic, palmitic, margaric, stearic, arachidic, eicosanoic, behenic, lignoceric, or cerotic acids, montanic acids, oleic, elaidic, erucic, linoleic, or linolenic acids, and also mixtures of acids which may be obtained from the natural fats and oils.

A special advantage of the release agents according to the invention is that the most favourable (physical) conditions for the intended shape and the plastic mass to be processed can be regulated through the starting substances used for its preparation. The (physical) condition of the release agents used according to the invention range from oily liquids to hard waxes. However, these differences in their consistency at room temperature do not result in any differences in their effect as lubricants. The actual physical condition of the products at room temperature is not effected by the size of the molecular weight, as is the case with monocarboxylic acid esters of simple structure. Further, the choice of dicarboxylic acid and polyol is also without substantial influence on the physical nature of the mixed esters used according to the invention at room temperature. On the other hand, whether the melting point value is high or low depends on whether the long-chain monocarboxylic acids used are preponderantly saturated or unsaturated in nature. Mixed esters, which contain as the monocarboxylic acid component exclusively saturated aliphatic monocarboxylic acids with 12 to 30 carbon atoms, are solid hard waxes with melting points of over 50°C. If on the other hand, unsaturated aliphatic monocarboxylic acids with 12 to 30 carbon atoms or mixtures of monocarboxylic acids with essentially unsaturated fractions as the monocarboxylic acid component are used for the preparation of the mixed esters, products are obtained which are oily liquids at room temperature and have solidifying points below 0°C. Thus, for example, a mixed ester from adipic acid, pentaerythritol and oleic acid has a solidifying point of −33°C, while a similarly constructed mixed ester, the monocarboxylic acid component of which is a partly unsaturated fatty acid mixture of chain lengths C_{16}—C_{18} with an iodine value of 50, has a solidifying point of −15°C.

In practical use the mixed esters from adipic acid, pentaerythritol and long-chain monocarboxylic acids with 12 to 30 carbon atoms, especially stearic and oleic acid, have proved the best of the release agents used according to the invention. The high molecular weight mixed esters based on the abovementioned three starting substances are of particular importance.

The release agents used according to the invention may all be added to the thermoplastic synthetic substances available for shaping, whether they be polymerisates, polycondensates or polyaddition products. The release agents are specially suitable for use in the shaping of chlorine-containing polymerisates, as for example, polyvinyl chloride, polyvinylidene chloride, and copolymerisates derived from vinyl chloride and vinylidene chloride. They can also be used, however, with advantage in the shaping of other plastics, such as for example, polystyrene, polyacrylic and polymethacrylic acid esters, polyamides and polyurethanes.

In practice, the said release agents are added to the thermoplastic masses to be processed before the shaping. The amount added depends upon the plastic to be processed and the kind of processing applied and generally varies from 0.01 to 5% by weight, preferably 0.05 to 2% by weight. After homogeneous distribution of the release agent in the plastic, the shaping can be effected by known processes.

The present invention will be further described by way of reference to the following specific Examples.

The mixed esters, all of which have an hydroxyl number of from 0 to 6, used in the following Examples were prepared as follows:

Product A: Mixed ester from maleic acid-pentaerythritol-behenic acid.

54 g of pentaerythritol (0.4 mol), 403 g of behenic acid (1.2 mol) and 0.75 g of tin dust were heated to 200—210°C in a three-necked round bottomed flask provided with a stirrer, a thermometer and a descending Liebig condenser: the said temperature being maintained for three hours. The removal of the water produced in the reaction was accelerated by the application of vacuum. After this time the triester of the pentaerythritol had been formed and the acid number had fallen to below 1. For the further reaction, 20 g of maleic anhydride (0.2 mol) and 0.25 g of tin dust were introduced into the melt cooled to about 150°C, and the latter was heated again for 3 to 4 hours at 180° to 200°C under vacuum. The final acid number of the crude ester was 2 to 3 and the yield was 434 g. The melt was subsequently bleached at about 100°C with 1% of fuller's earth and 1% of active charcoal. After cooling, a light caramel-coloured, easily grindable hard wax with a dropping point of 73°C was obtained.

Product B: Mixed ester from adipic acid-pentaerythritol-oleic acid.

73 g of pentaerythritol (0.5 mol), 338 g of commercial oleic acid (1.2 mol), 63 g of adipic acid (0.4 mol) and 1 g of tin dust were heated to 200—210°C in a three-necked round-bottomed flask fitted with a stirrer, thermometer and a descending Liebig condenser. After reaching this temperature a slight vacuum was applied, which was increased to about 20 mm Hg as the reaction progressed. The esterification was finished after 5 hours and the acid number had fallen to below 2. Bleaching with 1% of fuller's earth and 1% of active charcoal at 100—110°C and filtration were subsequently carried out. A yellow to wine-red oil with a viscosity of more than 1000 cP at 20°C was obtained. The solidifying point was −32°C and the flash point was 320°C.

Product C: Mixed ester from adipic acid-pentaerythritol-stearic acid.

68 g of pentaerythritol (0.5 mol), 405 g of commercial stearic acid (1.5 mol) and 1.2 g of tin dust were charged into a three-necked round-bottomed flask fitted with a stirrer, thermometer and a descending Liebig condenser, and the mixture was heated to 200—210°C and a low vacuum applied. This was increased to about 20 mm Hg in the course of four hours. After this time, the acid number had fallen to below 0.5. The product was cooled to about 150°C with stirring. The condenser was replaced by a water separator. After addition to the triester solution of 100 g of xylene, 36 g of adipic acid (0.25 mol) and a further 0.6 g of tin dust, esterification was completed under azeotropic conditions. Within four hours the calculated amount of water of reaction had been formed. The acid number was between 2 and 3. The xylene was distilled off under vacuum and the product was dried and bleached. A yellowish-white hard wax of dropping point 60°C was obtained.

Example 1

A mass consisting of 300 g of a polyvinyl chloride-suspension-polymerisate of K value 60 (Vinnol H 60 D (registered trade mark)) and 4.5 g of a thio-tin stabiliser (Advastab 17 M (registered trade mark)) for mixing, homogenising and production of a sheet, was processed on a rolling mill, the rollers of which had a breadth of 400 mm and a diameter of 220 mm, rotated at a speed of 12.5 r.p.m. and had a surface temperature of 180°C. The width of the gap between the rollers was adjusted so that the thickness of the rotating sheet was a uniform 0.6 mm. After running for 15 minutes, it was found that the mass adhered firmly to the surface of a roller and could not be detached. Now amounts (weights per cent) of release agent given in the following Table were added to the mass before placing on the roller mill and the mass mixed with the release agent was processed in the same way. The time which elapsed before the mass adhered thereby found represented a measure of the activity of the release agent. For comparison with the release agents used according to the invention, cetyl stearate was included in the experiment as a representative of known release agents.

The following values resulted, the values given being the number of minutes in which the release agent containing P.V.C. remained adhesive free during the processing:

Release Agent	Amount of release agent and freedom from sticking		
	0.1%	0.2%	0.3%
Cetyl stearate	15′	15′	15′
Product A	15′	85′	115′
Product B	45′	95′	105′

It is to be concluded from the Table that cetyl stearate as representative of the usual release agents shows no activity in the concentrations used, while with the release agents used according to the invention a considerable improvement in freedom from sticking is attained. The high molecular weight mixed ester Product B according to the invention, with an addition of 0.1%, already developed a distinct improvement of the freedom from sticking. With increasing additions, the action of Product A and Product B is about the same, but in every case is better than that of the comparative product.

Example 2

A mass from 300 g of a polyvinyl chloride-suspension-polymerisate of K value 60 (Vin-

nol H 60 D (registered trade mark)) and 4.5 g of a thio-tin-stabiliser (Advastab 17 M (registered trade mark)) was processed on a roller mill of dimensions 400×220 mm with a surface temperature of 180°C and a speed of 12.5 r.p.m. After running for 8 minutes the mass stuck fast to a roller and could no longer be drawn off. When 1.5 g of Product C were added to the mass before processing on the rollers, the mass could be worked for up to a time of 100 minutes without sticking. Within this time of treatment, after 30 and 60 minutes, a homogeneous smooth sheet of 0.3 mm thickness was removed. The sheet had great impact strength at room temperature and for the rest, showed the mechanical, electrical and chemical behaviour usual for plasticiser-free polyvinyl chloride.

Example 3

Batches of 100 parts by weight of a polyvinyl chloride polymeric mass of K value 57 (Hostalit M 3057 (registered trade mark)) were mixed in a high speed mixer with 4 parts by weight of a thio-tin-stabiliser (Advastab 17 M (registered trade mark)) and different amounts, indicated below, of a release agent. The powdered mixtures thus prepared were melted in an extruder with a cylinder diameter of 30 mm and a cylinder length of 750 mm. The extruder was equipped with a slot die 100 mm in width, in which shaping to a sheet of about 0.5 mm thickness was effected. The cylinder and die were kept at constant temperature by an electrical resistance heater. The speed was also kept constant at 30 r.p.m.

In a first experiment the mass to be processed contained 2.3 parts by weight of the stearic acid ester of a C_{12}—C_{20} alcohol fraction as the release agent. The torque necessary for melting and transporting the material amounted to 22.5 mkp and the axial screw back pressure was measured at 1780 kp. The plate issuing with a material temperature of 172°C showed flow lines on the surface and was transparent, but distinctly yellowish.

In a second experiment the mass to be processed contained only 1.5 parts by weight of the stearic acid ester of a C_{12}—C_{20} alcohol fraction and in addition 0.05 parts by weight of the product C as release agent. Under the same experimental conditions, only a torque of 8 mkp was necessary for melting and transporting the material and the screw back pressure was adjusted to 1500 kp. The plate issuing with a material temperature of 172°C possessed a completely smooth surface, which did not lose its brilliance even on relatively long storage. The plate was exactly as transparent as that obtained in the first experiment, but completely colourless.

The advantage which can be obtained by the addition of the release agents according to the invention during the processing or shaping of thermoplastic synthetic substances consists firstly in that the plastic masses show no tendency to stick to the parts of the machine even after long processing times. Further, shaped parts are obtained, the surfaces of which are marked by extraordinary smoothness, continuity and colour clarity, i.e. lack of yellowing. The shaped parts obtained can be further processed without difficulty by any known process such as bonding, welding, stamping, printing and lacquering.

WHAT WE CLAIM IS:—

1. A method of preventing sticking of thermoplastic synthetic material to parts of apparatus during processing of said thermoplastic material comprising adding to a mass of said thermoplastic material prior to processing 0.01 to 5% by weight based on the thermoplastic material of a release agent comprising a mixed ester having a hydroxyl and an acid number of from 0 to 6 and which is obtained from (a) an aliphatic, cycloaliphatic and/or aromatic dicarboxylic acid, (b) an aliphatic polyol and (c) an aliphatic monocarboxylic acid having from 12 to 30 carbon atoms in the molecule by an esterification reaction.

2. A method as claimed in claim 1 in which the polyol component of the mixed esters contains 2 to 6 hydroxyl groups in the molecule.

3. A method as claimed in claim 1 or 2 in which the dicarboxylic acid component of the mixed esters contains 2 to 22 carbon atoms in the molecule.

4. A method as claimed in any of the preceding claims in which the molar ratio of dicarboxylic acid : polyol : monocarboxylic acid is (n-1) : n : nm—2(n-1), in which *n* represents a whole number from 2 to 11 and *m* represents the functionality of the polyol.

5. A method as claimed in any of the preceding claims in which the mixed ester is derived from adipic acid, pentaerythritol and an aliphatic monocarboxylic acid with 12 to 30 carbon atoms in the molecule.

6. A method as claimed in claim 5 in which the mixed ester is derived from adipic acid, pentaerythritol and stearic acid.

7. A method as claimed in claim 6 in which the molar ratio of adipic acid : pentaerythritol : stearic acid in the mixed ester is n-1 : n : 4n—2(n-1), n representing a whole number from 2 to 8.

8. A method as claimed in claim 7 in which the ratio of adipic acid : pentaerythritol : stearic acid in the mixed ester is 1 : 2 : 6, 2 : 3 : 8, 4 : 5 : 12, 6 : 7 : 16 or 7 : 8 : 18.

9. A method as claimed in claim 5 in which the mixed ester is derived from adipic acid, pentaerythritol and oleic acid.

10. A method as claimed in claim 9 in which the molar ratio of adipic acid pentaerythritol : oleic acid in the mixed ester is n-1 :

n:4n—2(n-1), n representing a whole number from 2 to 7.

11. A method as claimed in claim 9 in which the ratio of adipic acid:pentaerythritol:oleic acid is 1:2:6, 3:4:10 or 5:6:14.

12. A method as claimed in any foregoing claim in which from 0.05 to 2% by weight, based on the amount of thermoplastic material, of said mixed ester is added to said mass of thermoplastic material.

13. A method as claimed in claim 1, substantially as hereinbefore described with reference to any of the foregoing Examples.

14. A thermoplastic synthetic substance having a content of a mixed ester as defined in any of claims 1 to 11.

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